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Reliable Electron Affinities of Perfluorocyclopropane and Perfluorocyclobutane from Convergent ab Initio Computations

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To resolve discrepancies concerning the magnitude of the electron affinities of perfluorocyclopropane and perfluorocyclobutane, quantum chemical calculations have been carried out with the MP2 and CCSD(T) methods in conjunction with augmented correlation consistent basis sets (aug-cc-pVX Z, X = D, T, Q). Though no experimental values have been found for perfluorocyclopropane, we estimate its electron affinity to be 0.17 eV (0.00 eV without zero-point vibrational energy corrections). In addition, determination of the electron affinity of perfluorocyclobutane (0.61 and 0.44 eV with and without zero-point vibrational energy corrections, respectively) is in good agreement with experimental values reported by Miller and co-workers (0.63 ± 0.05 eV). This study also demonstrates that the widely prescribed B3LYP/DZP++ model chemistry for computing electron affinities does not correctly describe these systems.

1. Introduction

Perfluorocycloalkanes are of importance in the microelectronics industry as etchant gases used in the manufacture of semiconductors.[1−5] Until recently, the negative ion states of the three smallest members of this class of compounds ($c\text{-}C_nF_{2n}$, $n = 3-5$) had not been definitively assigned.[6] A number of gas-phase studies have shown that electron attachment occurs to these compounds,[7−24] and theoretical studies support positive electron attachment to $c\text{-}C_3F_6$, $c\text{-}C_4F_8$, and $c\text{-}C_5F_{10}$.[6,22,23,25] However, agreement on the magnitude of the values has not been reached. To our knowledge, no experimental values for the electron affinity of perfluorocyclopropane ($c\text{-}C_3F_6$) have been reported. In addition, the only theoretical electron affinities for $c\text{-}C_3F_6$ were reported by our group,[6] but even those values varied substantially (0.02−0.57 eV, excluding zero-point vibrational energy (ZPVE) corrections).

The reported experimental values for perfluorocyclobutane ($c\text{-}C_4F_8$) vary widely, ranging from 0.52 ± 0.05 to 1.05 ± 0.10 eV. More than a decade ago, Miller et al. used rate constants of electron attachment to $c\text{-}C_4F_8$ in He to deduce EA($c\text{-}C_4F_8$) = 0.63 eV.[18] They were, however, unable to set error bars due to assumptions that had to be made in the experiment. Eight years later, Hiraoka et al. reported gas-phase ion/molecule reactions with SF_6^- and O_2^- that resulted in the assignment of two distinct electron affinities for $c\text{-}C_4F_8$ (1.05 ± 0.10 and 0.52 ± 0.05 eV, respectively).[22] They attributed the different values to the presence of a low-lying excited state. More recently, Miller and co-workers were able to assign error bars to their initial results through the use of a flowing-afterglow Langmuir-probe (FALP) apparatus.[23] This experiment yielded EA($c\text{-}C_4F_8$) = 0.63 ± 0.05, consistent with their previous result. Moreover, Miller argued that the larger value obtained by Hiraoka et al. was probably an experimental error due to the fact that SF_6^- has been known to be a poor electron-transfer agent.

Theoretical electron affinities of $c\text{-}C_4F_8$ range from 0.595 to 1.15 eV. While reporting their experimental values, Hiraoka et al. also used the B3LYP density functional with a double-ζ basis set to compute an electron affinity (including ZPVE corrections) of 1.15 eV.[22] More recently, Gallup reported a ZPVE corrected electron affinity of 0.640 eV from second-order Møller−Plesset perturbation (MP2) theory.[25] (Note that two of the three basis sets used by Gallup gave negative electron affinities, presumably due to the absence of diffuse functions.) Miller and co-workers also computed the ZPVE corrected electron affinities using B3LYP with a double-ζ basis set and G3(MP2) (0.942 and 0.595 eV, respectively).[23] Another recent paper reported ZPVE corrected electron affinites computed with both the B3LYP density functional (0.97−1.13 eV) and the MP2 method (0.60−0.82 eV). Note that the two methods differ by up to 0.5 eV.[6] Recognizing the wide range of experimental and theoretical electron affinities for $c\text{-}C_4F_8$ and the paucity of electron affinities for $c\text{-}C_3F_6$, this work examines $c\text{-}C_3F_6$, $c\text{-}C_4F_8$, and their negative ions with electronic structure methods as sophisticated as the CCSD(T) method and correlation consistent basis sets as large as aug-cc-pVQZ to reliably characterize the electron affinities of these species.

2. Computational Details

All geometries were obtained from the Cartesian coordinates provided in the Supporting Information of ref 6, which were optimized with either the B3LYP density functional or the MP2 method and the Huzinaga−Dunning TZ2P(*f*)+ basis set described therein. Both $c\text{-}C_3F_6$ and $c\text{-}C_3F_6^{\bullet-}$ structures belong to the D_{3h} point group whereas $c\text{-}C_4F_8$ and $c\text{-}C_4F_8^{\bullet-}$ are D_{2d} and D_{4h}, respectively. Figure 1 shows the structures of all four species considered in this study. Basis sets used in the current study include the Huzinaga−Dunning DZP+ and TZ2P(*f*)+ (see the Supporting Information of ref 6) and Dunning's series of correlation consistent basis sets augmented with diffuse functions on all atoms[26] (aug-cc-pVX Z, X = D,T,Q). The B3LYP[27,28] density functional, MP2[29], CCSD,[30−36] and CCSD(T)[37,38] methods were used to examine the effect of the treatment of dynamical electron correlation on the adiabatic electron affinities (EA_{ad}). The 1s-like core orbitals were excluded from the MP2, CCSD, and CCSD(T) correlation procedures (frozen core

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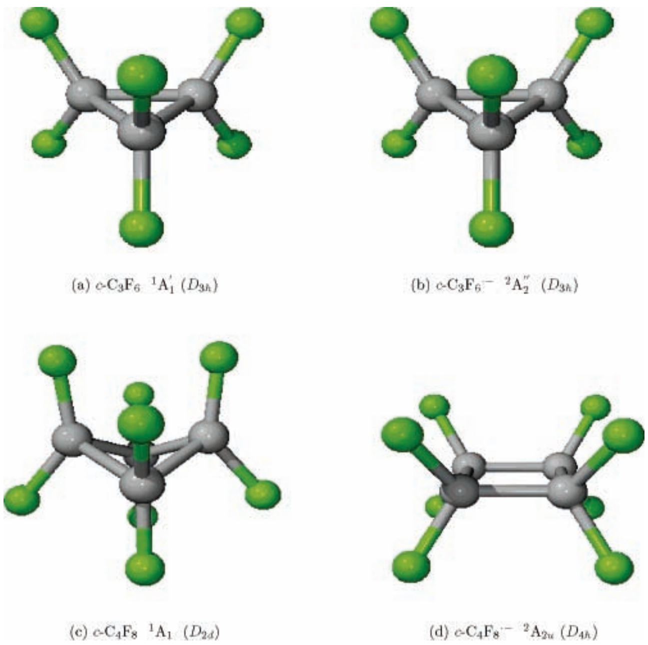
TABLE 1: Effect of Optimized Geometry on the EA_{elec} (eV)

method	geometry	c-C_3F_6	c-C_4F_8
B3LYP/DZP+	B3LYP/TZ2P(*f*)+	+0.47	+0.86
B3LYP/DZP+	MP2/TZ2P(*f*)+	+0.47	+0.89
B3LYP/TZ2P(*f*)+	B3LYP/TZ2P(*f*)+	+0.40	+0.80
B3LYP/TZ2P(*f*)+	MP2/TZ2P(*f*)+	+0.40	+0.82
MP2/DZP+	B3LYP/TZ2P(*f*)+	+0.11	+0.54
MP2/DZP+	MP2/TZ2P(*f*)+	+0.11	+0.51
MP2/TZ2P(*f*)+	B3LYP/TZ2P(*f*)+	+0.09	+0.54
MP2/TZ2P(*f*)+	MP2/TZ2P(*f*)+	+0.10	+0.52

TABLE 2: Effect of Spin Reference Function for the Anion (UHF vs ROHF) on the MP2 EA_{elec} (eV)

	c-C_3 F_6		c-C_4 F_8	
basis	UHF	ROHF	UHF	ROHF
DZP+	+0.12	+0.15	+0.58	+0.54
TZ2P(*f*)+	+0.10	+0.14	+0.53	+0.52
aug-cc-pVDZ	+0.31	+0.35	+0.75	+0.78
aug-cc-pVTZ	+0.14	+0.19	+0.59	+0.62
aug-cc-pVQZ	+0.16	+0.20	+0.61	+0.64



(a) c-C_3F_6 $^1A_1'$ (D_{3h}) (b) c-$C_3F_6^{\cdot-}$ $^2A_2''$ (D_{3h})

(c) c-C_4F_8 $^1A_1$ (D_{2d}) (d) c-$C_4F_8^{\cdot-}$ $^2A_{2u}$ (D_{4h})

Figure 1. Equilibrium structures, ground electronic states, and point group symmetries (in parentheses) of perfluorocyclopropane, perfluorocyclobutane, and their negative ions. The pucker of the c-C_4F_8 ring has been exaggerated to emphasize the D_{2d} structure.

approximation). For the DZP+ and TZ2P(*f*)+ basis sets, the 1s*-like orbitals were also excluded (deleted virtual approximation). The current study utilizes both the unrestricted and restricted open-shell Hartree−Fock references for the anionic species. The electron affinites (EA_{elec}) were computed as the electronic energy difference between the neutral molecules and their anionic counterparts. The EA_{ad} were computed in a similar manner and include the ZPVE corrections. We define the quantity $\delta_{MP2}^{CCSD(T)}$ as the difference between the CCSD(T) and MP2 EA_{elec}. All B3LYP calculations were performed with Gaussian 03,[39] and all other calculations were performed with the PSI3[40] program package.

3. Results and Discussion

In an earlier study of c-C_3F_6, c-C_4F_8, and their negative ions,[6] the optimized geometrical parameters showed little dependence on method and basis set. The ring puckering (measured as the torsional angle of the four ring carbons) in c-C_4F_8 was the only exception, where the puckering was approximately twice as large with the MP2 method as compared to the B3LYP density functional. To examine the effect of these geometrical differences on the electron affinities of these molecules, MP2 and B3LYP single point computations were performed on both sets of optimized structures. The results of these calculations are collected in Table 1. The effect of using B3LYP optimized structures when computing the MP2 electron affinities (or vice versa) is less than 0.03 eV. Clearly, the differences between B3LYP and MP2 optimized geometries are not responsible for the large variation in the computed electron affinities.

The choice of reference for the anionic species was also considered. Calculations involving both the unrestricted (UHF) and restricted open-shell (ROHF) Hartree−Fock references were performed with the MP2 method and five different basis sets (Table 2). The choice of reference has almost no impact on the computed EA_{elec}, changing the values by at most 0.05 eV.

Subsequently, CCSD and CCSD(T) single point calculations were carried out using a UHF reference for the anions. The MP2 and coupled-cluster data are presented in Table 3 along with the $\delta_{MP2}^{CCSD(T)}$ values. Note that in each case where it was possible to compute the CCSD(T) EA_{elec} (up to 420 basis functions), the $\delta_{MP2}^{CCSD(T)}$ terms are remarkably consistent and insensitive to basis set. Values in square brackets have been estimated by combining the MP2 EA_{elec} with the triple-ζ $\delta_{MP2}^{CCSD(T)}$ value. Although the CCSD(T) best estimate of the EA_{elec} of c-C_3F_6 is 0.00 eV, we note that our previous work reports zero-point corrections of 0.17 eV to the EA_{elec} of both c-C_3F_6 and c-C_4F_8 with a maximum deviation of ±0.02 eV. Thus, the inclusion of a harmonic ZPVE correction increases the electron affinity of c-C_3F_6 to 0.17 eV and that of c-C_4F_8 to 0.61 eV.

4. Conclusions

A series of systematic quantum chemical computations have been used to accurately determine the EA_{ad} of perfluorocyclopropane and perfluorocyclobutane. Estimates to the CCSD(T)/aug-cc-pVQZ adiabatic electron affinities are 0.17 and 0.61 eV, respectively (0.00 and 0.44 eV without ZPVE corrections). The

TABLE 3: EA_{elec} (eV) at Various Levels of Theory[a]

	c-C_3 F_6				c-C_4 F_8			
basis	MP2	CCSD	CCSD(T)	$\delta_{MP2}^{CCSD(T)}$	MP2	CCSD	CCSD(T)	$\delta_{MP2}^{CCSD(T)}$
DZP+	+0.12	−0.21	−0.07	−0.19	+0.58	+0.23	+0.37	−0.22
TZ2P(*f*)+	+0.10	−0.26	−0.06	−0.16	+0.53	+0.15	+0.35	−0.17
aug-cc-pVDZ	+0.31	−0.01	+0.16	−0.15	+0.75	+0.41	+0.59	−0.17
aug-cc-pVTZ	+0.14	−0.23	−0.02	−0.16	+0.59		[+0.42]	
aug-cc-pVQZ	+0.16		[+0.00]		+0.61		[+0.44]	
EA_{ad} best est[b]			+0.17				+0.61	

[a] Values in square brackets are assumed from results obtained with smaller basis sets. See text for details. [b] Includes a +0.17 eV ZPVE correction. See text for details.

latter value for c-C_4F_8 is in good agreement with the reported experimental values of Miller and co-workers. Because no experimental electron affinities for c-C_3F_6 has been found, our value is purely predictive in nature, but the small (nearly zero) values computed in this study may account for the absence of experimental data.

In addition, this study strongly suggests that the popular prescription of the B3LYP density functional and DZP++ basis set for electron affinities cannot correctly describe the electronic structure of these important perfluorocycloalkanes. This failure may be due to the unusual, highly delocalized nature of the singly occupied molecular orbital in the anion.[6] It is also worth noting that the CCSD method consistently and substantially underestimates the electron affinities by approximately 0.3 eV in all cases.

Note Added in Proof. During the review process a closely related work[41] was published that reports an adiabatic electron affinity of 0.60 eV for c-C_4F_8 from CCSD(T)/aug-cc-pVTZ computations (MP2/aug-cc-pVTZ optimized geometries and MP2/6-311G(*d*) ZPVE corrections) that is nearly identical to the value of 0.61 eV reported in this work.

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